

FT-IR DETERMINATION OF COAL AND SOOT PARTICLE TEMPERATURES DURING PYROLYSIS

Philip E. Best†, Robert M. Carangelo, and Peter R. Solomon, Advanced Fuel Research, Inc., 87 Church Street, East Hartford, CT 06108.

INTRODUCTION

The literature currently reports up to four orders of magnitude variation in the rate for coal pyrolysis at high temperature. The discussion of this problem with references to the literature is presented in (1,2). The wide variations appear to be caused by the inability to separate heat transfer from chemical kinetics. To resolve this issue, it is essential to measure particle temperatures in a pyrolyzing or combusting system. Several (two or more) color pyrometry systems have been developed for this purpose. A system which allows the measurement of single particle temperatures simultaneously with particle size and velocity was recently described by Tichenor et al. (3). The ability to measure temperatures of individual particles is important when there are temperature differences among particles. However, these systems have some disadvantages which limit their application. They employ wavelengths in the visible, which misses most of the emitted radiation. It is difficult to measure low temperatures (Tichenor et al. (3) estimate a 900 K limit for 10 micron particles) and to distinguish particle temperatures in the presence of soot or high temperature regions which can reflect radiation from the particle. Also, particle densities must be low, and it may sometimes be difficult to get a complete picture of a reacting system because low temperature particles will be overlooked.

The application of FT-IR emission and transmission spectroscopy is a good complement to the measurements in the visible, having advantages where the pyrometric techniques have disadvantages. It appears that contributions from soot and particulates can be separated by examining both the emission and transmission spectra and employing a knowledge of the soot's characteristic signature in the IR. Under conditions of uniform temperatures, particulate temperatures and soot densities can be determined. The FT-IR technique has advantages at low temperatures. At the temperatures of interest the emitted radiation has a maximum in the IR, providing good sensitivity. Also, because the measured spectrum covers the whole infrared range, the optical properties of the coal, char and soot (which vary in the infrared) can be measured and used to distinguish the nature of the particulates and the magnitude of reflected radiation. Finally, the technique can determine temperature for clouds of particles by comparing both the amplitude and shape of the emission and transmission spectra.

This paper discusses the application of the technique and preliminary results in a study of coal and acetylene pyrolysis.

EXPERIMENTAL

The emission of infrared light from, and transmission through, dispersed particles involves the processes of emission and absorption in the particle's interior, and reflection, diffraction and refraction at its surfaces. The infrared energy in these measurements can originate in the spectrometer, in the particles or from the hot experimental apparatus. To sort out these effects, as well as the influence of temperature, coal composition and morphology on the spectra, the studies described below have been carried out in a number of geometries.

Measurements In A Hot Cavity

Emission and transmission spectra were recorded in an entrained flow reactor (EFR) in which coal particles are fed into the furnace from a water cooled injector. In this geometry the coal "sees" hot furnace walls with the exception of the injector and the KBr windows that provide entrance and exit for the IR beam.

† permanent address: Department of Physics and Institute of Material Science, University of Connecticut, Storrs, CT 06268

Transmission spectra are recorded in the normal manner, as the ratio of transmission with and without the sample in the beam. In this experiment, the radiation from the spectrometer is amplitude modulated, so radiation originating from within the furnace is not detected. In the sample area, the beam geometry is identical for the emission and transmission experiments. In the emission experiment the detection sensitivity is wavelength dependent. The overall detection efficiency is measured by recording the spectrum from a cavity radiator of known temperature. The cavity serves both to provide a path correction at each wavenumber, and as a reference for the calculation of the shape and amplitude of black-body radiators of other temperatures. The reported emission spectra are also corrected for background.

An example of an emission spectrum for lignite in the furnace is presented in Fig. 1a. For the conditions at which each emission spectrum was recorded a corresponding transmission measurement was made, as shown in Fig. 1b which presents (1-transmission). Except for the gas lines, these spectra show a monotonic variation with wavenumber in a manner which can be accounted for by diffraction theory (2). Since we want to compare emission from particles which fill only a fraction of the viewing area with that from the cavity which fills 100% of the viewing area, we have computed a "normalized emission", Fig. 1c, in which the emission is divided by (1-transmission). The detailed significance of this "normalized emission" will be considered later. For the present we will discuss this function for the case in which the coal particles are of such size and texture that each one effectively blocks 100% of the radiation incident on it. In addition, we work in a dilute particle regime, so that less than 20% of the total beam is blocked. The particles can be considered to act as individual scatterers. In this case (1-transmission) is a measure of the projected area of the coal particles, and represents the fraction of the beam blocked by the sample. It also represents the projected emitting surface area as a fraction of the beam area. If we divide an emission spectrum by the corresponding (1-transmission) we obtain the spectrum that would appear if the sample completely filled the entrance aperture. We call these "normalized emission" spectra. The normalized spectra from a sample of black-body particles at temperature T would agree in shape and amplitude with the black-body spectrum corresponding to temperature T and generated from the information in the reference source spectrum. A similar set of emission, transmission and "normalized emission" spectra is presented for soot (Fig. 2). For sufficiently small soot particles the normalized spectrum can be rigorously equated to a black-body curve at the soot temperature. An appropriate theoretical black-body curve is also presented in Figs. 1c and 2c. Indeed, the "normalized emission" is quite close to the theoretical black-body in both shape and amplitude.

An example of normalized emission data, obtained for a lignite injected at several positions above the optical port in the EFR, is presented in Fig. 3. The data illustrate some of the potential benefits as well as the caution required in the interpretation. The figure shows the normalized emission spectra compared to a theoretical black-body curve at the window height wall temperature. Figure 3a presents data for coal injected just above the port. The coal at this position is cold. But there is obviously radiation emerging from the optical port which was not there in the absence of the coal. This must be scattered radiation. As the coal's residence time increases between injection and observation, the spectrum gets closer to the spectrum for the wall. At 36 cm the coal's absorption spectrum is gone, and the spectrum amplitude and temperature is higher than that of the wall. In this case the coal is cooling after having been heated to a higher temperature in the upper part of the furnace. This measurement without any further information can be used to determine the distance required for the coal to reach the reactor temperature.

For later purposes we have also reported the normalized emission from KCl particles in the EFR (Fig. 4).

Measurements In A Room Temperature Cavity

To allow separation of contributions from emission and scattering, a second geometry was used employing a tube furnace. In this experiment, the particles have been

heated in a high temperature tube prior to their coming into view of the IR beam. The turbulent environment of the tube convectively heats the coal particles very quickly ($>10^5$ K/sec). The only hot surface seen by the coal when it is in view is the overhead tube. Since the FT-IR spectrometer transmits only radiation which has its electric vector in the vertical plane, radiation from the tube scattered by one scattering event cannot be detected, in contrast to the case for the EFR experiment in which there is substantial scattering of wall radiations.

Figure 5 presents "normalized emission" spectra taken at the exit of the tube reactor after sufficient residence time to bring the coal up to the tube temperature. Each spectrum is compared with a black-body curve at the measured gas temperature at the position of the optical focus. At temperatures below 650 K, (Fig. 5a and b), only the region below 1700 wavenumbers has sufficient emissivity (absorptivity) to emit much radiation. As discussed later, the emissivity, ϵ_y , of the coal can be calculated from the data of Fig. 5 together with the extinction coefficient. We have calculated ϵ_y from the data of Fig. 5d and used it to compute the fraction of radiation from a 1800 K environment that is absorbed by the coal. The results indicate an equivalent grey-body emissivity of 0.2. Raw coal of pulverized coal size is, therefore, a poor emitter of radiation and consequently, is a poor absorber of radiation. It absorbs much less radiative energy than is usually computed assuming a grey-body with $\epsilon = 0.7$ to 1.0. This fact is important in computing the heating rate of the coal.

At temperatures of 750 K and 825 K the hydroxyl and aliphatic regions of the coal begin to emit (Figs. 5c and d). At 925 K, char condensation reactions are starting to produce a broad band emission as the char behaves more "graphitic"; this trend continues until, at 1200 K, the char is a grey-body with an emissivity between .7 and .8, similar to that of graphite.

Transmission And Reflection Measurements

Transmission measurements of coal in KBr pellets of coal films were recorded in a typical sample holder geometry for this experiment. The absorbances of two coal films of the same nominal thickness were measured. Figure 6a shows the spectrum of a uniform film of $1\mu\text{m}$ particles pressed into a KBr flat. The spectrum of Fig. 6b is for a film pressed at moderate pressure from a starting material of nominal $30\mu\text{m}$ diameter particles. Under an optical microscope the surface roughness of this latter film appeared comparable to that of an unpressed sample of the same coal. These spectra display the effect of morphology. The film made of ground ($1\mu\text{m}$) diameter particles has residual surface inhomogeneities of the order of the original particle size and can be expected to strongly scatter wavelengths in this region, with the scattering falling off as $(1/\lambda)$ towards longer wavelengths. In the region of 1800 cm^{-1} this $40\mu\text{m}$ thick film is moderately transparent. Extinction at longer wavelengths is due primarily to absorption, while at shorter wavelengths there is increased extinction due to scattering as well as absorption. For a film of similar thickness, but made of pressed $30\mu\text{m}$ diameter particles, (Fig. 6b) extinction over the long wavelength end of the spectrum is dramatically increased, showing qualitatively the dominance of scattering. The coal particles in our experiments have inhomogeneities more of the scale of the film of Fig. 6b than that of Fig. 6a: scattering plays a significant part in the interaction of the particles with radiation.

The specular reflection of coal was measured at an angle of incidence of 45° (Fig. 6c). This spectrum can be accounted for by standard theory using optical constants which lie within the range of published values (5). The reflection is small, (between 6 and 10%) and will be important only for rays which nearly graze the surface.

DISCUSSION

The scattering, absorption, transmission and emission of electromagnetic radiation from particles depend both on material properties in the form of the optical

constants, and on morphology, which can be represented by the scales of inhomogeneity relative to wavelength. The interaction of particles with the radiation field is characterized by efficiency factors, Q , which are the effective cross sections for scattering or absorption divided by the geometric cross section of the particles.

$$Q_{\text{ext}} = Q_s + Q_{\text{abs}} \quad (1)$$

where the subscripts stand for extinction, scattering and absorption, respectively (6). Q_s refers to radiation scattered out of the acceptance angle of the optics. Similarly, the other Q'_s are specific to our optical beam path. We will describe a simple model that semiquantitatively accounts for many features of the observed normalized emission spectra. The first feature of the model is due to the geometry of the experiment in the EFR. In this geometry, radiation from the transmission beam can scatter into almost a 360° solid angle of the furnace, while conversely, radiation from this almost 360° solid angle can scatter into the emission beam. The beam-defining aperture is just smaller than the furnace wall opening. For particles within the focus volume, for each incident beam 1 scattered into direction 2, we can find a beam 1' from the furnace wall that is scattered through the same angle into the original beam direction 2' (Fig. 7). From this discussion the following statement can be made about the relative scattering in emission and transmission experiments. If Q_s is the efficiency for scattering out of the beam path in a transmission experiment in this EFR, then

$$Q_s = Q'_s \quad (2)$$

where Q'_s is the efficiency for scattering wall radiation into the beam in an emission experiment, for particles within the focus volume. All the Q 's and ϵ 's that we subsequently discuss are wavenumber dependent but we have dropped the subscript, ν , for convenience.

If we observe the particle in an isothermal environment, then with the usual Kirchoff analysis, the radiation entering the optical aperture of the spectrometer would be

$$Q'_s \cdot BB(T) + \epsilon \cdot BB(T) = BB(T) \quad (3)$$

when the transmission through the particle is zero and where ϵ is the particle emissivity into the spectrometer acceptance angle, compared to the black-body emissivity of unity and where $BB(T)$ is the black-body spectrum corresponding to temperature T . As usual,

$$\epsilon = Q_{\text{abs}} \quad (4)$$

where both parameters refer to radiation entering or leaving the particle in the cone defined by the spectrometer aperture.

With these definitions we describe the normalized emission results as

$$\begin{aligned} & \frac{(\text{"observed emission"})}{(1-\text{transmission})} \\ & N_p \cdot A_p \cdot [\epsilon \cdot BB(T_p) + Q'_s \cdot BB(T_w)] \\ & = \frac{N_p \cdot A_p \cdot (Q_{\text{abs}} + Q_s)}{Q_{\text{abs}} \cdot BB(T_p) + Q_s \cdot BB(T_w)} \\ & = \frac{Q_{\text{abs}} + Q_s}{Q_{\text{abs}} + Q_s} \end{aligned} \quad (5)$$

where $BB(T_p)$ and $BB(T_w)$ are the black-body emission curves appropriate to the particle and EFR wall temperatures, respectively, N_p and A_p are the numbers of

particles in view, and their average geometrical cross-section, respectively. Equation 5 can be applied to explain the results of Figs. 1-5.

Case 1) If $Q_{\text{abs}} = 0$, as for KCl, the normalized emission should be equivalent in shape and amplitude to $BB(T_w)$, as is observed (Fig. 4).

Case 2) For soot particles of sufficiently small dimensions, the scattering is negligible (7). In that case the normalized emission (eq. 5) is given by $Q_{\text{abs}} BB(T_p) / Q_{\text{abs}} = BB(T_p)$. This predicts that the normalized emission from soot will be equal in amplitude and shape to the black-body curve corresponding to the soot temperature. This is indeed the case (Fig. 2). For KCl and soot, as well as all subsequent cases, there are no adjustable parameters in the comparisons we make.

Case 3) Another occasion in which a particularly simple result comes from this analysis is when the particle and wall temperatures are the same. Equation 5 shows that the normalized emission will be a good black-body curve, this time corresponding to the wall (and particle) temperature (Fig. 1).

The last cases to be considered are when non-black-body shape or amplitude is observed in the normalized emission (Figs. 3 and 5).

Case 4) Taking the case of the tube furnace first, and noting that there is no wall radiation to be scattered into the spectrometer in an emission measurement in that situation, the normalized emission is

$$\epsilon \cdot BB(T_p) / (Q_{\text{abs}} + Q_s) \quad (6)$$

For coal particles, the variation of the denominator of eq. 5 with wavenumber is similar to that of Fig. 1b: $Q_{\text{ext}} = Q_{\text{abs}} + Q_s$ has a value between 1 and 2, which can be estimated from diffraction theory (2). Multiplying the normalized emission by Q_{ext} , and dividing by the black-body curve corresponding to the measured temperature, gives an experimental estimate of ϵ , the coal emissivity. As expected from eq. 4, maxima in the emission in the tube furnace spectra (Fig. 5) correspond to maxima in the absorbance spectrum of the coal (Fig. 6).

Case 5) The most difficult case is for particles in the EFR where contributions come from both emission and scattering. In this case one can select regions of the spectrum which still permit simplification. For regions where the coal absorbs strongly (eg. 1600 cm^{-1}), Q_{abs} approaches unity for sufficiently large particles. Such regions of the spectrum can be used to determine the particle temperature.

CONCLUSIONS

Normalized FT-IR emission spectra appear to contain a considerable amount of information about the solid phases in pyrolyzing coal and gas systems. In this preliminary work we have deduced solid phase temperatures for a number of circumstances, demonstrated the ability to detect chemical change in high temperature reactions, and deduced a grey-body emissivity for coal. With improved evaluation of how the emissivity changes with pyrolysis, there are good prospects that the temperature determining capability of the method can be extended.

ACKNOWLEDGEMENTS

This work was supported by the U. S. Department of Energy, Morgantown Energy Technology Center under Contract No. DE-AC21-81FE05122, U.S. Department of Energy, Pittsburgh Energy Technology Center under Contract No. DE-AC22-82PC50254 and The National Science Foundation under Contract No. CPE-83-60666.

REFERENCES

1. Solomon, P.R., Hamblen, D.G., Carangelo, R.M., Markham, J.R., and DiTaranto, M.B., ACS Division of Fuel Chemistry Preprints 29, #2, p. 3 (1984).
2. Solomon, P.R. and Hamblen, D.G., Finding Order in Coal Pyrolysis Kinetics, Progress in Energy and Combustion Science, 9, 323 (1983).
3. Tichenor, D.A., Mitchell, R.E., Hencken, K.R. and Niksa, S., Simultaneous In-Situ Measurement of the Size, Temperature and Velocity of Particles in a Combustion Environment, presentation at the 20th Symposium (Int) Conference on Combustion; Aug. 12-17, 1984, University of Michigan, Ann Arbor Michigan.
4. Gumbrecht, R.O. and Sliepcevich, C.M., J. Phys. Chem. 57, 90 (1953).
5. Foster, P.J. and Howarth, C.R., Carbon, 6, 719, (1968).
6. van de Hulst, H.C., Light Scattering by Small Particles, Dover Publications, NY, (1981).
6. D'Alessio, A., Cavaliere, A. and Menna, P., Soot in Combustion Systems, Edited by J. Lahaye and G. Prado, Vol. 7, pg. 327, (Plenum Press, NY), (1983).

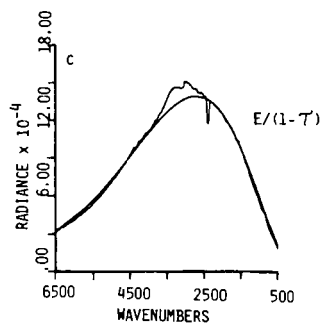
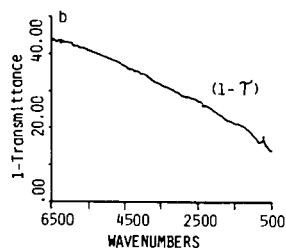
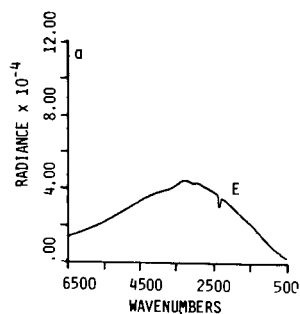
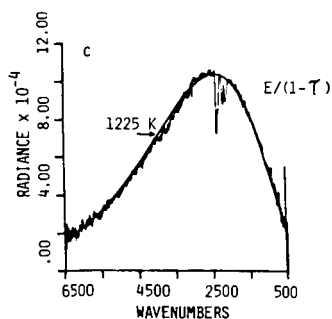
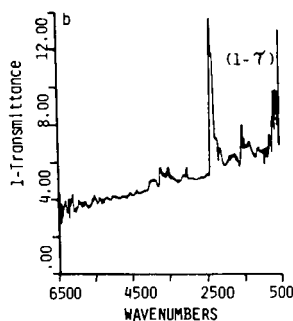
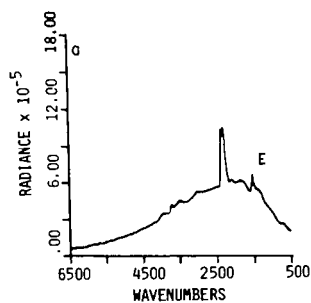


Figure 1. a) Emission, b) (1-transmission), and c) $E/(1-T)$, Curves for a Lignite (mesh size -300 +425) Injected into the Furnace at 36 cm above the Window. Furnace Wall Temperature at Window Height is 1170 K.

Figure 2. a) Emission, b) (1-transmission), and c) $E/(1-T)$, Curves for Soot formed by Acetylene Injected into a Furnace at a Height of 66 cm above the Window. Furnace Wall Temperature is 1250 K. Curve c is a Quantitative Black-body Curve Corresponding to a Temperature of 1350 K.

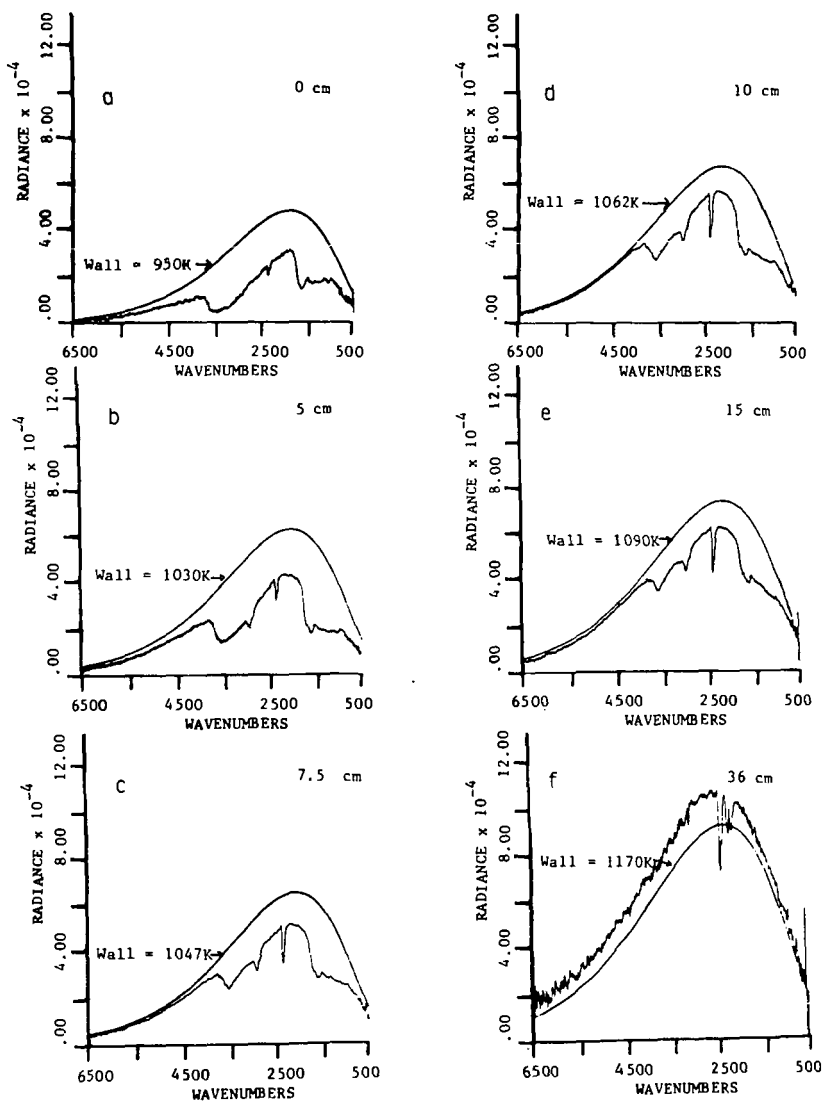


Figure 3. Series of $E/(1-T)$ Curves for Lignite Particles in the Furnace for Increasing Residence Time.

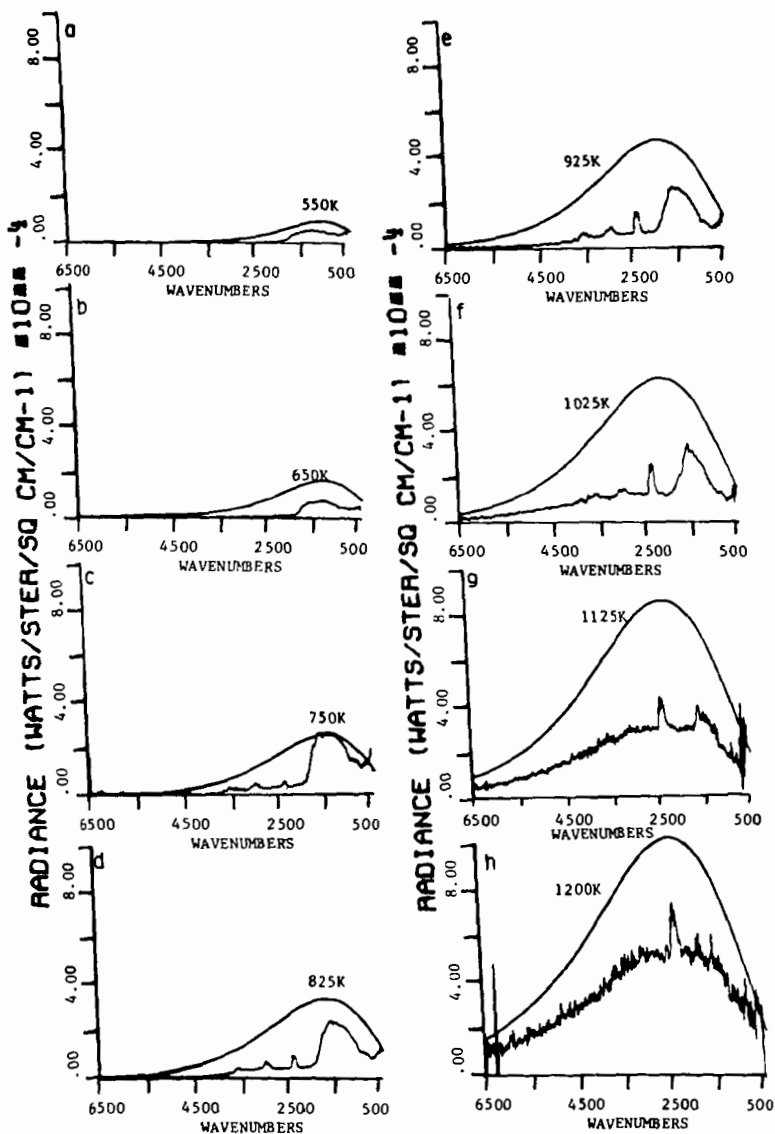


Figure 5. Series of Emission Normalized by (1-transmission) for Lignite Particles in the Tube Reactor for Increasing Temperature.

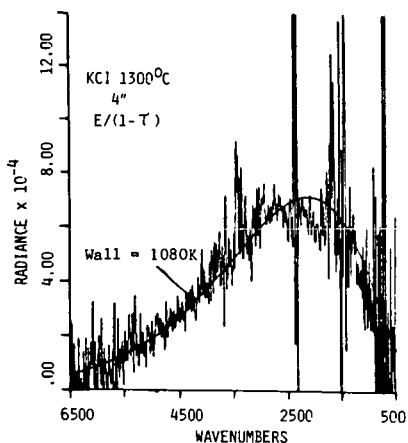


Figure 4. $E/(1-T)$ for Cold KCl Particles in a Hot Furnace. Furnace Wall Temperature is 1080 K. This Curve is a Quantitative Black-body Curve Corresponding to a Temperature of 1080 K.

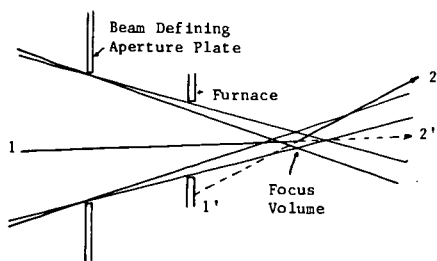


Figure 7. Configuration of Beam Defining Aperture and Furnace Wall in EFR.

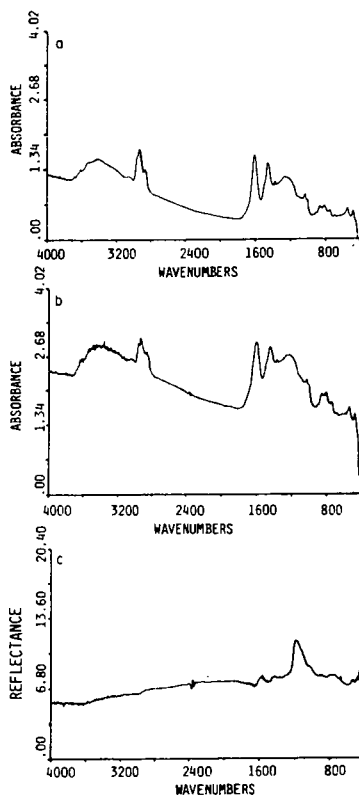


Figure 6. a) Spectrum of 40 μ m Coal Film Pressed from 1 μ m Diameter Particles, b) Spectrum of 40 μ m Coal Film Pressed from 10 μ m Particles, and c) Specular Reflection of a Coal Pellet Pressed from 1 μ m Diameter Particles.